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(21) International Application Number: PCT/RO99/00001 (22) International Filing Date: 11 January 1999 (11.01.99) (71) Applicant (for all designated States except US): S.C. ZECASIN S.A. [-/RO]; Splaiul Independentei 202, R-77208 București 6 (RO). (72) Inventors; and (75) Inventors/Applicants (for US only): POP, Grigore [RO/RO]; Str. Timișoara 17B-106B, ap. 32, sc. A, R-7000 București 6 (RO). GANEA, Rodica [RO/RO]; Șso. Ștefan cel Mare 38-30A, ap. 68,, sc. B, R-7000 București (RO). IVANESCU, Doina [RO/RO]; Șso. Ștefan cel Mare 15-15; ap. 8, s. c. F; R-7000 București (RO). IGNATESCU, Gheorghe [RO/RO]; Alcea Portișa 2-13, ap. 24, sc. B, R-Ploiești (RO). BOERU, Rodica [RO/RO]; Str. Târnave 1-A1, ap. 82, sc. F, R-Ploiești (RO). BÎRJEGA, Ruxandra [RO/RO]; Str. Aviator A. Popovici 6A-6, ap. 14, R-7000 București (RO). (74) Common Representative: S.C. ZECASIN S.A.; Splaiul Independentei 202, R-77208 București 6 (RO).		(81) Designated States: AU, BR, CA, CN, GE, HU, ID, JP, KR, MX, NO, NZ, PL, SI, TR, US, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims and statement.</i>
(54) Title: CATALYTIC PROCESS FOR THE PREPARATION OF LIGHT OLEFINS FROM METHANOL IN A FLUIDISED BED REACTOR (57) Abstract Methanol is converted in light molecular olefins C ₂ -C ₄ with 93-100% degree of transformation and more than 90% selectivity in which more than 80% are ethylene and propylene upon a microspherical catalyst based on SAPO-34 zeolite, with continuous reaction-regeneration in a fluidized bed reactor-regenerator system. Ethylene/propylene ratio is changed in relatively large limits, 0.69-1.36, by the modification of reaction temperature and space velocity of the feed.		

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CATALYTIC PROCESS FOR THE PREPARATION OF LIGHT OLEFINS FROM METHANOL IN A FLUIDISED BED REACTOR

Background of the Invention

Field of Invention

This invention relates to a process for conversion of methanol to olefins using SAPO-34 zeolite in fluidized bed reactor with continuous regeneration of catalyst.

Background Art of the Invention

Light olefins, namely ethylene and propylene, are important raw materials for polymers production.

Industrial, ethylene and propylene are obtained by steam cracking of C_2-C_4 paraffins and petroleum fractions in so called hydrocarbons pyrolysis process. The continuous rising of olefins requirement with the oil reserve shortage in the future make interesting the researches for new olefins manufacture technologies from non petroleum raw materials.

One of the more attractive method for C_2-C_4 olefins production is based on catalytic conversion of methanol because methanol is manufactured in advanced technologies with very high capacity till 800,000 mt/year a single line and has wide raw materials availability like natural gases including methane, coals and renewable biomass.

Methanol conversion into light olefins with industrial accepted yields was possible only after the synthesis of high silica zeolite ZSM-5 by Mobil Oil's researchers (U.S. Patent 3.702.886). After this many other types of zeolites were tested in the reaction of methanol to olefins like ZSM-34 (US Patent 4079096), Mordenite (Ro Patent 87685, US Patent 3244766), Offretite (US Patent 4079096) arseno-silicates (Ger. Off. 2830830), boro-silicates (Ger. Off. 2830787). Methanol conversion to olefins is claimed also in many patents based on synthetic alumino-silicates like US Patents 4062905, 3979472, 3911041 and Ger. Off. 2755299, 2615150.

These catalysts exhibit low selectivities in olefins and must be periodically regenerated with air at 470-570 °C.

Numerous methods for modification of zeolites and reaction conditions were elaborated for olefins selectivity rising and increasing the active cycle of the catalysts. Interesting results were obtained by zeolite silification (US Patent 4100219, 4145315), increasing Si/Al atomic ratio by aluminium extraction (US Patent 4447669, Ger. Off. 2935863), ionic exchange or impregnation with Cs, Ba, Pb, Tl (US Patent 4066714), B, Mg (US Patent 4049573, Ger. Off. 3300892), Hf, Zr (US Patent 4481376, Ger. Off. 3300982), dilution of the catalyst with inert materials (US Patent 4025572), partial deactivation with steam (UK Patent 2127036) or HF (US Patent 4486617). Good results have given complex treatments with Mg-Mg or Mg-Sb (RO Patent 87413). Some reaction parameters were also modified, for instance under atmospheric pressure utilization (US Patent 4025575), steam dilution of feed (US Patent 4083889) or dilution with air (US Patent 4433189), oxygen (US Patent 4049735) and aldehyde (US Patent 4374295).

The synthesis by Union Carbide Corporation's researchers of Si-Al-P zeolites named SAPO-zeolites (US Patents 4310440, 4440871) has opened new perspectives for methanol conversion to olefins, MTO-process. As the Chinese researchers have demonstrated for the first time onto SAPO-34 zeolite it obtained till 89% C₂-C₄ olefins at practical total conversion of methanol 57-59% being ethylene and ethylene/propylene molar ratio 2.24-2.31 (Applied Catalysis, Vol. 40, Nr. 1-2, 1988, p.316). Due to the catalyst coking active cycle is only 1-2 hours.

The use of SAPO-34 zeolite synthesised as in US Patent 4440871 rose contradictory literature data concerning the thermal and steam stability and olefins selectivity. It must be also underlined that the synthesis of the zeolite is made with expensive materials like aluminium isopropoxide, tetraethylammonium hydroxide or quinuclidine. Neutralization of the reaction mixture with NaOH has complicated the technology for SAPO-34 manufacture due to the necessity of ammonium ion exchange and supplementary calcination step.

Thermal analysis (Gr.Pop et al., Progress in Catalysis, Bucharest, 1, 1993, p.1) showed that a good thermal and steam stability have SAPO-34 zeolites with crystals smaller than 4 micrometer.

MTO - process was materialized in tubular reactors with fixed bed catalyst (US Patent 4590320) and in fluidized bed reactors with catalyst regeneration in fluidized bed. Vaporized methanol feed mixed with the zeolite catalyst is charged to the bottom of the riser contact zone to form a suspension for flow upwards through the riser (U.S. Patent 4328384). The reactors with fixed bed catalyst have many disadvantages in methanol reaction to olefins because the removal of the reaction heat is difficult and frequent catalyst regeneration diminishes production capacity. The increasing of the coke deposits on the catalyst in the active cycle changes continuously the reaction products composition.

Fluidized bed reactors and continuous regeneration of the catalyst eliminate these disadvantages but in a riser reactor the optimal reaction conditions can't be realized.

Kinetic studies in fluidized bed reaction have shown the maximum ethylene formation at short reaction time of about two seconds. (C. Tsakiris et al., Proc. IFAC Symposium DYCORG 92 College Park, Maryland, April 1992), which is not obtainable in a riser reactor. In a riser type reactor two important reaction parameters, contact time and temperature, determining product selectivities can't be well controlled.

Summary of the Invention

The Invention eliminates these difficulties since the catalyst is obtained from cheap raw materials like industrial alumina and aqueous silica sol and the template, tetraethylammonium phosphate is "in situ" prepared: by ethylbromide and triethylamine. The methanol conversion and continuous catalyst regeneration are conducted in fluidized bed reactors, without riser, methanol feed being injected in dense bed catalyst.

Detailed description of the Invention

The catalyst synthesis is made only with cheap, industrial raw material namely triethylamine, ethyl bromide, concentrated phosphonic acid, more than 70 weight %,

hydrated alumina and silica sol, all with very low, under 0,01% Na content. Concentrated silica sol can be stabilized with ammonia. In the condition of the patent, by hydrothermal treatment of Si-Al-P amorphous gel is obtained the active, H form of SAPO-34 zeolite, in relatively short zeolitization time. After the calcination at 350-580 °C for remove the organic template, the obtained zeolite is used as catalyst. The zeolite is atomized at 400-450 °C in a silica matrix as microspheres. The composition of amorphous gel and the reaction condition in the crystallization, calcination and atomization steps assure to obtain an active and selective catalyst for methanol conversion to olefins, with a granulation curve suitable in a fluidized bed process and with good thermal and mechanical resistance.

The process of methanol conversion to light olefins mainly ethylene and propylene, is realized in fluidized bed, including a reactor - regenerator system, with continuous circulation of the coked catalyst from reactor to regenerator and the regenerated catalyst from regenerator to reactor. The methanol feed and regeneration air are injected in the dense bed of the catalyst. This system assures constant temperature in the catalyst beds and contact time of about two seconds. The reactor and regenerator risers only hinder the fluxes reversing. By steam or nitrogen purging in the risers, the catalyst is purified by the methanol and hydrocarbons adsorbed in reactor and oxygen adsorbed in regenerator. So the loss of methanol by burning in regenerator is avoided. Also is avoided the burning of the methanol in the reactor by the oxygen adsorbed on the catalyst in regenerator. The purging of the catalyst assures a very low carbon oxides in the reaction products with a supplementary reduction of the costs for olefins separation. To keep constant the catalyst activity a small amount is removed from reactor or regenerator in parallel with adding an equal quantity of fresh catalyst. The reactor and regenerator have interior devices for taking-over the heat reactions of methanol conversion and coke burning.

The following examples illustrate, but not limit, the present invention.

Examples

Example 1

By known method is prepared a tetraethylammonium phosphate, aqueous solution 25%, from triethylamine, ethylbromide and phosphoric acid 73%.

Hydrated alumina 65% Al_2O_3 with 40% bayerite, is suspended in demineralized water and is charged, under stirring in a 3500 l autoclave over tetraethylammonium phosphate solution and then is added the 28% SiO_2 silica sol stabilized with ammonia. The pH of resulted suspension is fixed at 6,3-6,5 with phosphonic acid.

Molar ratio of the component in the suspension is:

P_2O_5 : Al_2O_3 : SiO_2 : TEAOH 1:1.5:0.37:1.1.

Zeolitization is made in six successive steps: the first step of the crystallization begins with 15% of the whole suspension at 198-205 °C. After 20 hours the autoclave is cooled at 30-40°C and a new quantity of suspension is added. The zeolitization process is resumed in the same conditions. The operation is repeated five times. The entire zeolitization process, including intersteps cooling, is about 100 hours.

Analytical control, by XRD technique, of the product obtained shows more than 90% SAPO-34 zeolite and about 7% unreacted bayerite.

In Table 1 are shown the characteristic bands in the XRD - spectrum of the SAPO-34 zeolite obtained, and SAPO-34 spectrum reported in U.S. Patent No. 4440871, for comparison.

Table 1. Characteristic bands in XRD-spectrum
(Cu lamp, Cu k_{α} = 1.5418)

U.S. Patent No. 4440871			Sample, Example 1		
2 θ	d, Å	100 Xi/I ₀	2 θ	d, Å	100 Xi/I ₀
9.45-9.65	9.36-9.17	81-100	9.63	9.18	100
12.8-13.05	6.92-6.78	8-20	12.87	6.88	18
13.95-14.20	6.35-6.24	8-23	14.17	6.25	21
16.0-16.2	5.54-5.47	25-54	16.16	5.4	47
17.85-18.15	4.97-4.89	11-26	18.3	4.89	22
19	4.67	0-2	-	-	-
20.55-20.9	4.32-4.25	44-100	20.67	4.3	97
22.05-22.50	4.03-3.95	0-5	22.33	3.98	4
23.0-23.15	3.87-3.84	2-10	23.15	3.84	8
24.95-25.4	3.57-3.51	12-87	25.38	3.52	26
25.8-26.0	3.45-3.43	14-24	25.97	3.43	17
27.5-27.7	3.243-3.220	1-4	27.68	3.22	4
28.05-28.4	3.181-3.143	1-12	28.4	3.14	4
29.2-29.6	3.058-3.018	3-9	29.15	3.06	4
30.5-30.7	2.931-2.912	19-75	30.67	2.91	29
31.05-31.4	2.880-2.849	15-28	31.25	2.86	22
32.2-32.4	2.780-2.763	1-5	32.42	2.76	3
33.4-33.85	2.683-2.648	0-6	33.66	2.66	4
34.35-34.65	2.611-2.589	4-15	34.48	2.6	7
36.0-36.5	2.495-2.462	2-11	36.33	2.47	4
38.8-38.9	2.321-2.315	0-2	38.8	2.32	2
39.6-39.7	2.276-2.070	2-4	39.76	2.27	5

The crystallite dimensions are between 1 and 3 micrometer (Figure 1). The zeolite is stable by calcination and in air and steam, as is shown in Figure 2.

In the zeolitization phase results a zeolite suspension with 16.7% solid which is separated with 6.7 l/m² hours filtration rate. After washing with demineralized water and air drying results a paste of zeolite with 57% humidity.

The humid paste of zeolite is mixed with 28% SiO₂ Silica sol stabilized with ammonia in weight ratio zeolite: SiO₂ 60-40, fixed at pH 6.3 with nitric acid 40% and atomized under pressure with 400-450 °C hot air at entrance and 175-180 °C at exit. Injection pressure is 4-4.5 bars and the productivity of atomizer 50 kg/hour dry catalyst. Finally the catalyst is calcined with a heating rate of 100 °C/min. at two

constant level, three hours at 350-400 °C and ten hours at 580 °C. The cooling time of the catalyst is 4 hours. All the raw material used for catalyst preparation has a Na content under 0,01%. The microspherical catalyst obtained has good flow property and granulation curve showed in Figure 3.

Figure 4 is a schematic flow chart of the reaction - regeneration with fluid bed catalyst system for methanol conversion to olefins, MTO process, part of invention. With reference to Figure 4, the reactor R1 is filled with 100 l catalyst and the regenerator R2 with 30 l catalyst. By fluidization is taken from the dense fluid bed catalyst 2-2' and upper interface 3-3'. The temperature of dense fluid bed catalyst in R1 is fixed at 440 °C and in R2 at 480-610 °C. The temperatures in R1 and R2 are controlled by circulating heating - cooling agent in interior heat exchangers 9-9'. Methanol and regenerating air are fed through connection 5-5' and sieves 4-4' with 100 l/hour respectively 1000 Nl/hour.

The circulation of the catalyst between reactor and regenerator is realized by nitrogen as lift gas through transfer lines 12-12'. Automatic control level of catalyst bed in R1 and R2 is made by keep constant the pressure drops with regulators 11-11', which act the catalyst flow rate regulating valves 10-10'. Reaction products and catalyst entrained are evacuated at the top of R1 and R2 and separated in cyclone systems 6-7 and 6'-7'. Through the conduits 8-8' the entrained catalyst is recycled in the reactor-regenerator reaction zone. About 2 kg catalyst is withdrawn from the bottom of separation cyclone 7 or 7' in each 48 hours and is replaced with the same quantity of fresh catalyst through the charge device 15 or 15'. So the irreversible desactivation of the catalyst is compensated.

The coked catalyst in the conduit 13 has 4.3 wt.% coke and the regenerated catalyst in conduit 13' has a coke retention level of 1.7 wt.%. Reaction products after the exit from cyclone 7 are cooled in heat exchanger 14 and separated in the separation vessel 16 into a noncondensed hydrocarbon fraction and a liquid fraction which contains the process water, dimethylether and unconverted methanol. The gaseous hydrocarbon fraction is sent to a conventional olefins separation unit. From liquid fraction is separated by distillation dimethylether and methanol which are recycled to the reactors R₁.

Regeneration gases after cooling in heat exchanger 16' and washing in the column 14' are evacuated in the atmosphere.

The composition of the fluxes are shown in Table 2.

Table 2. Effluent composition obtained in Example 1.

Component	Uncondensed organic phase vessel 16 wt. %	Liquid phase vessel 16 wt. %	Regeneration gases, exit cyclone 7' wt. %
Oxygen	-	-	1,5
Nitrogen	-	-	82.7
Carbon monoxide	-	-	4.3
Carbon dioxide	-	-	11
Hydrogen	0.2	-	0.5
Methane	1.6	-	-
Ethane	0.3	-	-

Component	Uncondensed organic phase vessel 16 wt. %	Liquid phase vessel 16 wt. %	Regeneration gases, xit cyclone 7' wt. %
Ethylene	46.8	-	-
Propane	2.5	-	-
Propylene	40	-	-
Butanes	0.53	-	-
1-Butene	1.74	-	-
iso-Butene	0.71	-	-
2-Butenes	4.04	-	-
C ₅ + hydrocarbons	1.58	-	-
Methanol	-	0.5	-
Dimethylether	-	-	-
Water	-	99.5	-

Example 2

Using the catalyst and installation of Example 1 by temperature and space velocity modification the ethylene/propylene ratio is changed in relatively large limits of 0.69-1.29.

Some illustrating results are shown in Table 3.

Table 3. Reaction products compositions, in different reaction conditions.

Experience number	1	2	3	4	5	6
a. Reaction conditions						
Temperature, °C	400	405	410	435	470	490
LHSV, h ⁻¹	1.1	0.6	1	1.9	1.5	2.7
b. Uncondensed organic phase analysis, wt. %						
Hydrogen	0.08	0.23	0.13	0.12	0.71	0.1
Carbon oxydes	-	-	-	0.14	0.21	-
Methane	0.62	1.78	0.81	1.12	2.42	0.91
Ethane	0.26	0.9	0.42	0.64	-	-
Ethylene	28.3	48.5	34.1	43	42.45	36.8
Propane	2.3	5.3	2.4	2.43	5.9	2.27
Propylene	41.2	35.7	42.9	42	32.95	45.4
Butanes	0.9	0.88	0.8	0.68	0.8	0.72
1-Butene	1.94	1.19	1.75	1.63	1.94	1.7
iso-Butene	0.77	1.23	0.75	0.44	1.04	0.2
2-Butenes	7.22	2.56	6.68	4.87	7.13	5.2

REFERENCES

1. Brent M.Lok, Celeste M. Messina, Robert L. Pation, Richard T. Gajek, Thomas R. Cannan, Edith M. Flanigen (Union Carbide Corporation), U.S. Patent No. 4440871 (April 3, 1984), Int. Cl. B01 j 27/14; U.S. Cl 502/241.
2. Ajit V. Sapre (Mobil Oil Corporation); U.S. Patent No.4590320 (May 20, 1986), Int. Cl. Co7C1/20; U.S. Cl.585/324; 585/315
3. Nicholas Davidiuk, James Haddad (Mobil Oil Corporation) U.S. Patent No. 4328384 (May 4, 1982), Int. Cl. C 97c1/20, U.S. Cl. 585/469; 585/639; 585/733.

Experience number	1	2	3	4	5	6
C5 +Hydrocarbons	2.41	0.95	2.84	1.58	4.45	1.75
Dimethylether	14	0.78	6.42	1.35	-	4.95
c. Liquid phase analysis, wt.%						
Dimethylether	1.5	-	0.5	-	-	-
Methanol	12	3	9	1.5	0.1	1.5
Water	86.5	97	90.5	98.5	99.9	98.5
d. Coke deposits on the catalyst, wt.%						
Reactor R1 exist	4.9	5	4.8	4.5	4.6	4.7
Regenerator R2 exit	1.2	2.8	0.6	0.9	1.2	1.9
e. Ethylene / propylene ratio	0.69	1.36	0.79	1.02	1.29	0.81
f. Methanol conversion	93.3	98.3	95	99,2	100	99.2

What is Claimed is

1. Method of light molecular olefins production by methanol conversion using microspherical SAPO-34 zeolite in matrix as catalyst, wich comprises: the preparation of the zeolite by hydrothermal treatment in absence of Na⁺ ions, using as crystallization agent tetraethylammonium phosphate and the conversion of methanol to light olefins in fluidized bed catalyst at 400-490 °C and liquid space velocities 0.6 to 2.7 h⁻¹, by injection of the feed in dense bed of catalyst.

2. The method of claim 1 wherein the activity and selectivity of the catalyst are kept constant by continuous regeneration, with air, at 480-610 °C and by fresh catalyst addition with simultaneous withdrawl from the reaction-regeneration system of an equawly quantity of used catalyst.

3. The method of claims 1,2 wherein unreacted methanol and dimethylether are separated and recycled in the reaction phase.

4. The method of claims 1,2,3 wherein the ethylene/propylene ratio in reaction product is modified in the limits 0.69-1.36 by the change of reaction temperature and the space velocity of the feed.

AMENDED CLAIMS

[received by the International Bureau on 05 October 1999 (05.10.99);
original claim 1 amended; new claim 5 added; remaining claims unchanged. (1 page)]

Experience Number	1	2	3	4	5	6
C ₅ + Hydrocarbons	2.41	0.95	2.84	1.58	4.45	1.75
Dimethylether	14.00	0.78	6.42	1.35	-	4.95
c. Liquid phase analysis, wt. %						
Dimethylether	1.5	-	0.5	-	-	-
Methanol	12	3	9	1.5	0.1	1.5
Water	86.5	97	90.5	98.5	99.9	98.5
d. Coke deposits on the catalyst, wt. %						
Reactor R ₁ exit	4.9	5	4.8	4.5	4.6	4.7
Regenerator R ₂ exit	1.2	2.8	0.6	0.9	1.2	1.9
e. Ethylene/propylene ratio	0.69	1.36	0.79	1.02	1.29	0.81
f. Methanol conversion	93.3	98.3	95	99.2	100	99.2

What is claimed is: -

- Method for light molecular olefins production by methanol conversion using microspherical SAPO-34 zeolite in matrix, as catalyst, which comprises:-
 - the preparation of the zeolite by hydrothermal treatment, in the absence of Na⁺ ions;
 - stepwise correction of the pH-value with phosphoric acid;
 - using, as crystallization agent and raw material for phosphorus the tetraethylammonium phosphate;
 - the conversion of methanol to light olefins in fluidized bed catalytic reactor at 400 – 490°C, liquid space velocities of 0.6 – 2.7 h⁻¹ by injection of the feed in the dense bed of a fluidized bed catalytic reactor or in a moving bed catalytic reactor.
- The method of Claim 1 wherein the activity and selectivity of the catalyst are kept constant by continuous regeneration, with air, at 480 – 610°C and by fresh catalyst addition with simultaneous withdrawal from the reaction-regeneration system of the same quantity of used catalyst.
- The method of Claims 1 and 2 wherein the unreacted methanol and dimethylether are separated and recycled in the reaction stage.
- The method of Claims 1, 2 and 3 wherein the ethylene/propylene ratio in the reaction product is modified in the range 0.69 – 1.36 by changing the reaction temperature and/or the space velocity of the feed.
- The method of claim 2 wherein the coke content of the catalyst at the exit from the regenerator is kept under 4%wt.

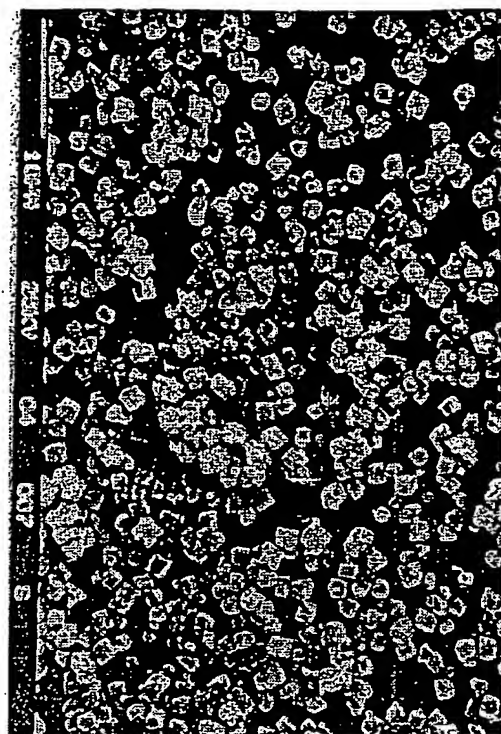


Figure 1. SEM microphotography of Exemple 1 zeolite

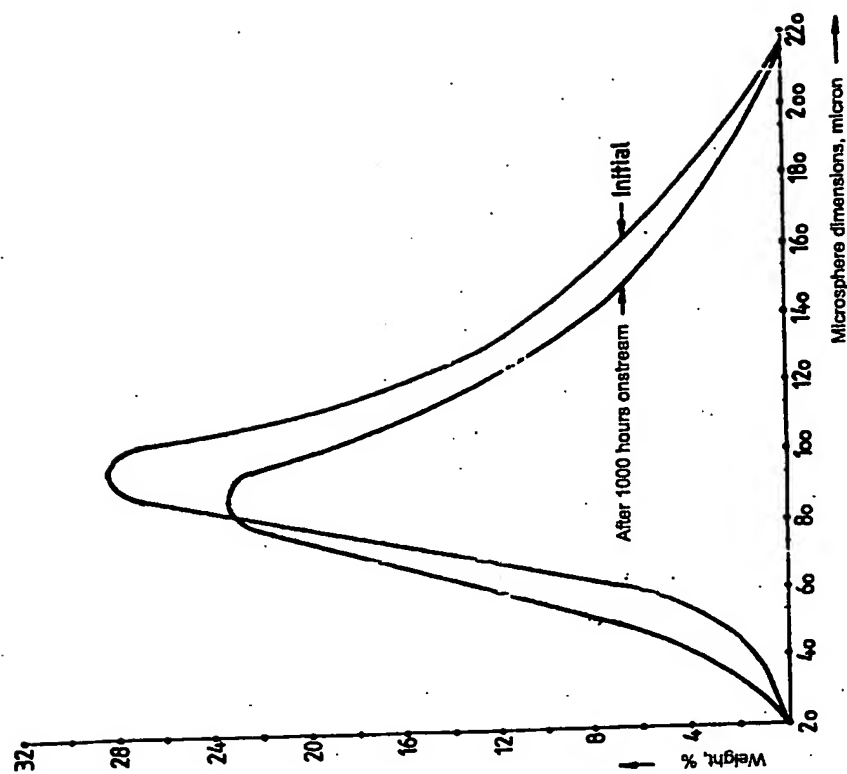


Figure 3. Dimension distribution curves of the catalyst, Example 1

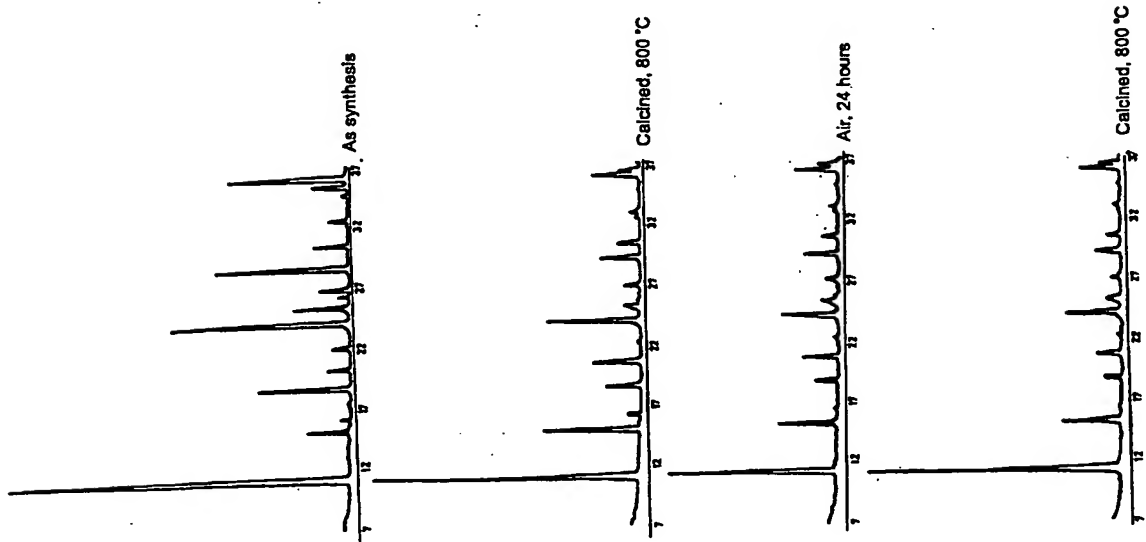


Figure 2. XRD-spectra of Example 1 sample

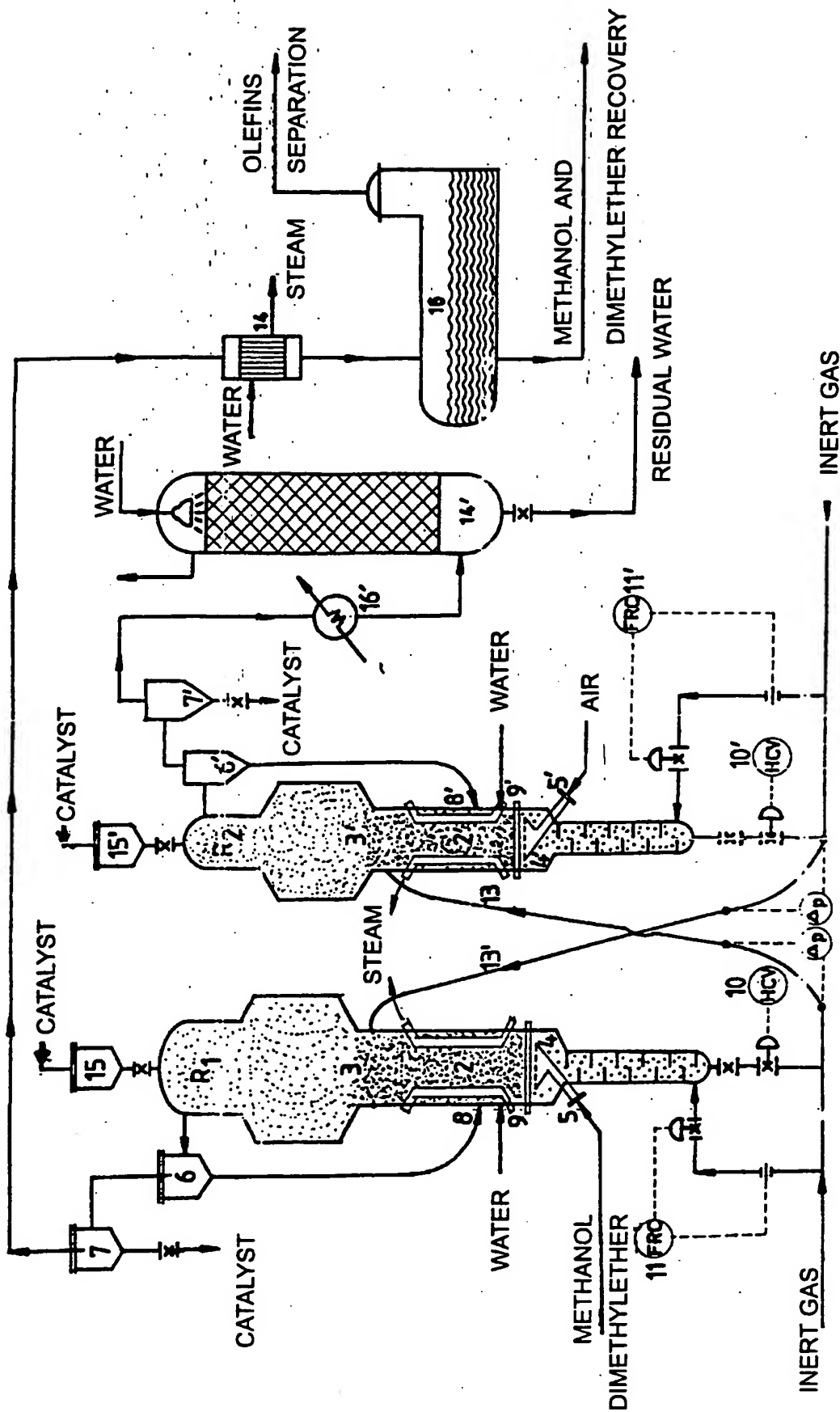


Figure 4. Installation for methanol conversion to olefins

INTERNATIONAL SEARCH REPORT

Int. National Application No.

PCT/RO 99/00001

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C11/02 C07C1/20 B01J29/85

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 095 163 A (BARGER PAUL T) 10 March 1992 (1992-03-10) examples	1-4
X	US 4 873 390 A (LEWIS JEFFREY M O ET AL) 10 October 1989 (1989-10-10) examples	1-4



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